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<p>(54) Title: CELL WALL LOADING OF NEVER-DRIED PULP FIBERS</p>		
<p>(57) Abstract</p> <p>There is disclosed a filled paper composition comprising intact cellulose fibers and fillers wherein the cellulose fibers are originally never-dried, and wherein the filler material is in an insoluble precipitate formed <i>in situ</i> within the cell wall of the never-dried cellulose pulp fibers. The filled paper composition is characterized by having increased strength characteristics relative to a corresponding conventionally loaded paper composition containing the same amount of the same filler material. There is also disclosed a process for the production of filled paper using never-dried pulp fibers and filler comprising an insoluble precipitate that is precipitated <i>in situ</i> within the cell wall of the fibers. The process first immerses the never-dried pulp fibers in a first solution containing a soluble salt or salts, filters the pulp fibers from the first solution, and reimmerses the never-dried pulp fibers containing the first solution in the pores into a second solution, wherein the second solution comprises soluble salt or salts different from those of the first solution and able to form an insoluble precipitate with the salt or salts of the first solution. The filled, never-dried pulp fibers are filtered and washed and either used to form filled paper products or dried to filled pulp fibers for later use in papermaking.</p>		

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Description

CELL WALL LOADING OF NEVER-DRIED PULP FIBERS

5

Technical Field of the Invention

This invention relates to a filled paper composition wherein the filler is an insoluble precipitate predominantly located within the cell wall of never-dried cellulosic pulp fibers. The location of the filler within the cell walls determines the resulting filled paper composition having increased strength relative to a corresponding conventionally filled paper containing the same amount of the same filler.

The present invention also relates to a process for producing a filled paper composition having increased strength relative to a conventionally filled paper having the same concentration of the same filler material.

Background of the Invention

The increasing cost of virgin pulp and the energy associated with its transformation are familiar problems to most papermakers. The boom in hardwoods utilization, the optimization of high-yield pulping processes, and the ongoing conversion to alkaline sizing are only a few examples of many attempts made in recent years to address papermaking problems. The most economically useful approach has been to replace pulp fibers with cheaper filler materials. High-filler papers are also called ultrahigh-ash paper when calcium carbonate (CaCO_3) is the filler. However, the major constraint of ultrahigh-ash paper is an impairment of interfibrillar bonding. This results in decreased paper strength.

Papermaking processes often use fillers or opaque pigments to confer some desirable characteristics to the paper product and to provide a cost savings for paper raw materials. Fillers can increase opacity, brightness and printing properties. Fillers are cheaper substitutes than cellulose fibers and can reduce the total cost of the finished paper product. Moreover, fillers can be dried easier than fibers and reduce energy consumption during the papermaking process.

10 An essential property of paper for many end uses is its opacity. It is particularly important for printing papers, where it is desirable to have as little as possible of the print on the reverse side of a printed sheet or on a sheet below it be visible through
15 the paper. For printing and other applications, paper must also have a certain degree of brightness, or whiteness. For many paper products, acceptable levels of optical properties can be achieved from the pulp fibers alone. However, in other products, the inherent
20 light-reflective characteristics of the fibers are insufficient to meet consumer demands. In such cases, the papermaker adds a filler.

A filler consists of fine particles of an insoluble solid, usually of a mineral origin, suspended
25 in a slurry. By virtue of the high ratio of surface area to weight (and sometimes high refractive index), the filler particles confer light-reflectance to the paper and thereby increase both opacity and brightness. Adding fillers to paper pulp produces an enhancement of
30 the optical properties of the paper and further produces the advantages of improved smoothness and improved printability. Further, replacing fiber with an inexpensive filler can reduce the cost of the paper. However, filler addition poses some additional problems.

35 One problem associated with filler addition is that the mechanical strength of the paper is less than could be expected from the ratio of load-bearing fiber

to non-load-bearing filler. The mechanical strength of paper can be expressed in terms of burst index, tear index, and tensile index. The usual explanation for this is that some of the filler particles become trapped
5 between fibers, thereby reducing the strength of the fiber-to-fiber hydrogen bonding. The hydrogen bonding is the primary source of paper strength.

There exists a practical limit to the amount of filler which can be used. The paper mechanical
10 properties depend primarily upon hydrogen bonding between fibrous elements. Filler accumulates on the external surface of the fibers. Accumulated filler weakens the paper strength. Further, one must use increasing amounts of retention aids to avoid excessive
15 pigment losses through the paper-forming wire. Accordingly, filler concentrations are often limited to a maximum of about 10% ash content.

Several techniques have been used to try to overcome the problems of decreased strength from
20 increasing filler content. Most approaches have involved filler surface modification, using retention additives, and using supplemental bonding agents. For example, preflocculated fibers and fillers have been used to increase filler retention and reduce loss of
25 paper strength. Coarser particles of pigment or filler, caused by the preflocculation procedure, are retained more efficiently than the finer particles of pigment. Thus, there is less interference with inter-fiber bonding. This helps improve paper strength. However,
30 paper opacity is reduced with increasing particle size. Moreover, the cost savings associated with the preflocculation technique are insignificant and are offset by additional problems.

Craig, U.S. Patent No. 2,583,548 ("Craig"),
35 describes a process forming a pigmented cellulosic pulp by precipitating pigment "in and around" the fibers. According to Craig, dry cellulosic fibers are added to a

solution of one reactant, for example, calcium chloride, and the suspension is mechanically worked so as to effect a gelatinizing of the dry fibers. A second reactant, for example, sodium carbonate, is added so as to effect the precipitation of fine solid particles, such as calcium carbonate. The fibers are then washed to remove the soluble by-product (sodium chloride).

The Craig process has considerable limitations. The presence of filler on fiber surfaces and the gelatinizing effect on the fibers are detrimental to paper strength. The gelatinized fibers are so severely broken that both the filler precipitate and the gelled fibers form a slurry. Thus, the Craig process has not achieved commercial success despite its disclosure about 39 years ago.

Another technique is described in U. S. Patent No. 4,510,020. This process has been called the "lumen-loading" process and it involves placing the filler material directly within the lumens of soft wood pulp fibers. "Lumen-loaded" pulp is prepared by vigorously agitating a dry softwood pulp in a concentrated suspension of filler. The action of the agitation encourages the filler to move through transverse pit apertures in the fiber cell walls and into the lumen, where the filler material is adsorbed against the surface of the lumen cavity. Subsequent washing of the lumen-filled pulp fibers rapidly eliminates residual filler from the external surfaces of the fibers but only slowly from the lumen. The result is an increased retention of filler within the lumen, while removing the hindrance to inter-fiber bonding by removing the filler outside of the fiber lumens. The result is increased paper strength for the amount of filler present. The lumen-loading technique works best with fibers that have been dried.

The lumen-loading technique, however, has not proved to be economically or commercially viable. The

technique requires the manipulation of large volumes of relatively concentrated filler suspensions agitated at high revolutions for prolonged periods of time. Further, the lumen-loading technique requires a
5 relatively small particle size filler, such as titanium oxide, which is an expensive filler material. Moreover, the lumen-loading technique will only work for dry softwood fibers having a sufficient number of pit apertures. As the lumens are open at the pits, filler
10 may be lost in the same way that it is introduced. Further, the pores in the cell walls are not filled by the lumen-loading technique.

Accordingly, there is a need in the art to be able to produce economical paper of high opacity and
15 strength using as much filler material as possible, and to be able to use cellulosic pulp fibers from any source (e.g., softwoods, hardwoods and annual plants, such as sugarcane).

20 Summary of the Invention

The present invention refers to a filled-paper composition comprising intact, never-dried cellulose fibers and filler, wherein at least 50% of the filler content is located within the pores or cell wall of the
25 never-dried cellulose fibers. The filled paper composition is characterized by having increased strength compared to a corresponding conventionally filled paper containing the same amount of the same filler. The filler is formed in situ as an insoluble
30 precipitate in an aqueous system. The paper composition may further comprise a coloring agent wherein the coloring agent is a colored precipitate formed in situ that functions as a filler material.

Examples of insoluble precipitates that
35 function as filler materials include, for example, calcium carbonate, other precipitates listed in Table 1 herein, and combinations thereof. The paper composition

is selected from the group consisting of unbleached kraft paper, bleached kraft paper, sulfite pulp (bleached and unbleached) fine printing paper, fine writing paper, and lightweight newsprint paper.

5 The invention further describes a process for the production of filled paper wherein the starting pulp is a never-dried pulp. The inventive process comprises dispersing the never-dried pulp in a first solution, wherein the first solution comprises a salt or salts, to
10 form a first dispersion; filtering the pulp from the first dispersion; and redispersing the filtered, never-dried pulp in a second solution to form a second dispersion, wherein the second solution comprises a salt or salts different from the salt or salts of the first
15 solution and with the proviso that the interaction of the salt or salts from the first solution and the salt or salts from the second solution form an insoluble precipitate that acts as a filler within the pores of the cell wall of the never-dried pulp. This forms a
20 filled pulp fiber that can be filtered and dried or used wet for papermaking.

The paper is made by further process steps known to those of ordinary skill in the art. The pulp can be used directly for papermaking without drying, or
25 dried as filled pulp fibers and later used for papermaking.

The present invention includes a filled paper product made from filled, never-dried cellulose pulp fibers, wherein the filled paper is made directly from
30 the filled, never-dried pulp or the filled, never-dried pulp is made, dried, and later used to make paper. The essential steps of the inventive process are as follows:

1. Immersing (or dispersing) the never-dried pulp in a first solution, wherein the first solution
35 comprises a soluble salt or salts;

2. Filtering the immersed, never-dried pulp and then redispersing (or reimmersing) the filtered,

never-dried pulp in a second solution, wherein the second solution comprises a soluble salt or salts different from the soluble salt or salts of the first solution and with the proviso that the interaction of
5 the salt or salts from the first solution and the salt or salts from the second solution form an insoluble precipitate in situ that acts as a filler within the cell wall or pores of the never-dried pulp; and

3. Filtering and washing the filled never-
10 dried pulp.

The paper can be made directly with the filled, never-dried pulp fibers by conventional procedures. Alternatively, the filled, never-dried pulp can be dried and later used for papermaking.

15 In another embodiment, the filled, never-dried pulp fibers are beaten after filling in the never-dried state or after being once dried. If the unbeaten, filled pulp is dried, the papermaker can control the specifications of the beating process in the papermaking
20 operation.

The never-dried cellulose pulp can be derived from hardwoods, softwoods, annual plants such as sugarcane (bagasse), and combinations thereof.

The present invention is able to load a
25 precipitate-type filler material within the cell walls or pores located within the cell walls of never-dried pulp fibers by the internal in situ precipitation of insoluble fillers and pigments. Never-dried pulp fibers are unique in having relatively large-sized pores
30 located within the interior of the cell wall. These pores collapse when the pulp fiber is dried and are not fully restored by the rewetting of the dried fiber. Therefore, one can optimally precipitate filler material within the cell wall surrounding the lumen only before
35 the fiber is dried. Similarly, filled fibers, filled by the inventive process and dried, cannot be refilled by the inventive process.

Filler materials, such as pigments and opaque precipitates, are loaded into the pores of the cell walls of never-dried wood pulp fiber by precipitating the filler material inside the pores. This replaces the fluid content of the pore. Excess filler is washed away from the external surface of the fiber and an insignificant amount, if any, of filler material remains within the lumen of the fiber. As never-dried pulp fibers are hollow, tubular structures, the fibers develop an extremely large surface area after pulping and retain that large surface area while remaining wet (i.e., never-dried). The large surface area within the never-dried fibers is generously available to soluble salts that are precipitated as papermaking fillers. This preserves the bonding ability of the external cellulosic layers and does not affect the strength of the resulting paper.

Brief Description of the Drawings

Figure 1a is a scanning electron micrograph at 2142X magnification showing the surface of filled, never-dried pulp fiber filled according to the inventive process with NiCO_3 insoluble precipitate filler. Figure 1b is an electron dispersion analysis (EDAX) of the filled fiber showing Ni location and distribution in the cell wall of the fiber.

Figures 2a, 2b, and 2c are EDAX graphs of Ni (07 box) of a NiCO_3 -filled, never-dried pulp fiber showing the surface of the fiber, the cell wall of the fiber, and the fiber lumen, respectively. Filler was predominantly present in Figure 2b, indicating the presence of nickel in the cell wall.

Figures 3 and 4 illustrate the tensile index and burst index, respectively, of different filler content papers made from never-dried western hemlock pulp (a softwood). The filled circles represent paper made from fibers filled by the inventive process, and

the open circles or squares represent paper made from fibers filled by a conventional process, as described in Example 1. The different symbols represent different batches run on different dates.

5 Figures 5, 6 and 7 illustrate tear index, burst index, and tensile index, respectively, for different filler content papers made from red alder pulp (a hardwood). The open circles or squares represent the inventive process with CaCO_3 as the filler precipitated
10 in situ, wherein, for the open squares, CaCl_2 was the first salt and Na_2CO_3 was the second salt, and for the open circles, Na_2CO_3 was the first salt and CaCl_2 was the second salt. The closed triangles are data from paper made from mixtures of cell wall filled and
15 unfilled fibers in ratios of 1:3, 1:1, and 3:1, respectively. The open diamonds are red alder, never-dried pulp fibers filled by the conventional techniques described in Example 1. The "x" designation used once-dried red alder pulp, rewetted and filled by the
20 inventive process.

Figures 8, 9, and 10 illustrate the tear index, burst index, and tensile index, respectively, for different filler content papers made from spruce CTMP pulp (a softwood). The open squares represent in situ
25 precipitated, never-dried pulp fibers filled by the inventive process. The open circles represent never-dried pulp fibers loaded in a filled paper by a conventional process described in Example 1.

Figures 11, 12, and 13 illustrate the tear
30 index, burst index, and tensile index, respectively, for different filler content papers made from bagasse pulps (sugarcane). The filled squares represent in situ precipitated, never-dried pulp fibers filled by the inventive process, with the filled squares being
35 bleached pulp and the open squares being unbleached pulp. The diamonds represent never-dried pulps filled by a conventional process, as described in Example 1,

with the filled diamonds being bleached pulp and the open diamonds being unbleached pulp. The triangles represent once-dried, bleached pulp filled by the inventive process. The poor results obtained with the
5 once-dried pulps indicate that pores of the never-dried pulp fibers are necessary to be able to fill the cell walls of fibers.

Figure 14 compares the relative decrease in tensile strength as a function of filler content
10 comparing literature data of the lumen-loading technique (triangles or "x" figures) to never-dried pulps filled by the inventive process using red alder hardwood pulp (open squares), bagasse sugarcane pulp (diamonds), and spruce CTMP softwood pulp (closed circles).

15

Detailed Description of the Invention

Never-dried pulp is formed by removing the lignin and hemicellulose from cellulose wood fibers during pulping. The pulp obtained is a composite of
20 several hundred concentric lamellae of cellulose microfibrils. Each lamella is separated from the others by water-filled spaces (pores) which vary in width from about 25 to about 300 angstroms. The larger spaces are located nearer the periphery, with the narrower spaces
25 located toward the lumen (a central channel of about 10 to about 20 microns in width). The spacing of the pores more or less corresponds to the thickness of the lignin in the cellulose wood fiber. The pore size generally has a normal log distribution. A surprising result of
30 the inventive process is that most of the first solution leaves the fiber lumen when the fiber is filtered between the addition of the first and second solutions. This is because the lumen is more open to the external environment than the pores in the cell wall. Thus,
35 little, if any, filler is precipitated in situ in the lumen. The normal log distribution of pore size is a

plot of the logarithm of the pore size versus pore frequency.

The never-dried pulp fiber has a surface area of about 1,000 m²/g. Upon drying, the surface area
5 reduces to about 1 m²/g. Even though the lamellae swell upon rewetting, the rewetted pulp has a surface area of only about 100 m²/g. Thus, upon drying, most of the pores of the never-dried pulp irreversibly collapse.

The inventive composition and processes depend
10 upon the special properties of the never-dried pulp or its equivalents. The never-dried pulp has a large internal surface area of about 1,000 m²/g as a result of the corresponding internal cell wall pore volume of about 1.2 mL/g. The internal cell wall pores are
15 substantially lost by collapse during drying. Anything placed within the pores before drying becomes trapped in the pores, as the pores collapse during drying.

We have shown that if never-dried pulp is sequentially treated with a first solution containing a
20 soluble salt, such as calcium chloride, and filtered to remove the soluble salt from the exterior of the fiber and the lumen, and then a second soluble salt, such as sodium carbonate, is added, the filler, calcium carbonate, is created within these pores but not within
25 the lumen. This process is appropriate for other filler materials when the filler is an insoluble precipitate formed from the interaction of two or more soluble salts.

When the filler is located within the cell
30 wall by the in situ process, interference with the hydrogen bonding between fibers is reduced. As a consequence, the strength of paper made from such in situ precipitation cell wall-filled fibers is greater than the strength of paper made from the usual
35 (conventional) combination of fibers and the same amount of filler particles added to the fibers, when the filler. The conventional mixture of filler and fibers

locates the filler between the fibers. Furthermore, if the filler is located inside the cell wall of the fiber in the inventive process and compositions, the abrasive filler will have less contact with the forming wire on the paper machine. This will result in fewer wire changes being needed for the paper machine in a given period of time. Moreover, there is a reduced opportunity for filler to dust off from the paper sheet because the filler is located predominantly within the cell wall of the fibers rather than outside of the fibers.

Another advantage of the inventive process and compositions is that larger amounts of filler are used to form paper and maintain the strength of the resulting paper. The paper filler does not require incorporating adhesive polymers to maintain paper strength. Thus, paper made using the inventive process without adhesive fillers can have larger amounts of filler than conventionally made paper, while retaining equal or superior strength characteristics. Since filler is generally more economical than pulp fibers, the inventive process provides an economic benefit by a lower cost of goods for the finished paper composition. Moreover, it is less energy intensive and more economical to dry filler than to dry fiber. Thus, reduced energy costs for paper forming will be achieved by reduced drying costs.

The inventive process takes never-dried pulp and precipitates a filler material in situ. In one embodiment, never-dried pulps are filled by consecutively soaking the never-dried pulp in solutions comprising a soluble salt or salts. The never-dried pulps are first soaked in a first solution for approximately five minutes or less. The first solution comprises a soluble salt or salts and functions to replace the water within the pores in the cell wall and in the lumen with a solution containing the soluble salt

or salts of the first solution. The never-dried pulp fibers are filtered and washed, which removes the salt or salts from the first solution from the exterior and the lumen of the fibers. A second solution containing a
5 different soluble salt or salts is added to the filtered fibers. The interaction of the salt or salts from the first solution within the pores of the cell wall of the never-dried pulp fibers and the soluble salt or salts of the second solution forms an insoluble precipitate that
10 falls out of solution within the pores of the cell wall of the never-dried pulp fibers. The precipitate within the cell wall of the never-dried pulp fibers acts as a filler. When the fibers are dried or used to make paper and later dried, the insoluble precipitate acts as paper
15 filler. The filled, never-dried pulp fibers are subsequently filtered and washed and used to form paper. Alternatively, the filled fibers may be dried and shipped to a papermaking facility as dry lap.

Pulp fibers are often beaten to certain
20 specifications as part of the papermaking procedure. The beating of the pulp fibers occurs before forming the paper. The inventive process allows the beating to occur either before or after filling the fibers. Moreover, never-dried pulp fibers can be filled, dried
25 and then beaten before use to form paper.

The order of the soluble salts in the first or the second solution is not important to the process. What is important is that the salt or salts of the first and second solution be different and that they form an
30 insoluble precipitate upon interaction. Examples of white (opaque) and various colored precipitates are listed in Table 1.

TABLE 1

EXAMPLES OF PRECIPITATES USED AS FILLERS

<u>Color</u>	<u>Name</u>	<u>Formula</u>
5	<u>White</u> Calcium chloride	CaCl_2
	Aluminum phosphate	AlPO_4
	Zinc ammonium phosphate	$\text{Zn}(\text{NH}_4)\text{PO}_4$
	Calcium phosphate	CaPO_4
	Magnesium ammonium phosphate	$\text{Mg}(\text{NH}_4)\text{PO}_4$
10	Calcium borate	$\text{Ca}(\text{BO}_2)_2$
	Bismuth phosphate	BiPO_4
	Magnesium carbonate	MgCO_3
	Zirconium hydrogen phosphate	$\text{Zr}(\text{HPO}_4)_2$
	Zirconyl hydrogen phosphate	$\text{ZrO}(\text{H}_2\text{PO}_4)_2$
15	Aluminum hydroxide	$\text{Al}(\text{OH})_3$
	Bismuth hydroxide	$\text{Bi}(\text{OH})_3$
	Zinc hydroxide	$\text{Zn}(\text{OH})_2$
	Titanium hydroxide	$\text{Ti}(\text{OH})_4$
	Zirconium hydroxide	$\text{Zr}(\text{OH})_4$
20	Calcium silicate	CaSiO_3
	Barium sulfate	BaSO_4
	Barium silicofluoride	BaSiF_6
	Barium hydroxide	$\text{Ba}(\text{OH})_2$
	Barium orthophosphate	$\text{Ba}_3(\text{PO}_4)_2$
25	Barium pyrophosphate	$\text{Ba}_2\text{P}_4\text{O}_7$
	Barium metasilicate	BaSiO_3
	Barium carbonate	BaCO_3
	Bismuth oxycarbonate	BiO_2CO_3
	Cadmium carbonate	CdCO_3
30	Calcium metaborate hexahydrate	$\text{Ca}(\text{BO}_2)_2 \cdot 6\text{H}_2\text{O}$
	Calcium hydroxide	$\text{Ca}(\text{OH})_2$
	Calcium orthophosphate	$\text{Ca}_3(\text{PO}_4)_2$
	Calcium pyrophosphate pentahydrate	$\text{Ca}_2\text{P}_2\text{O}_7 \cdot 5\text{H}_2\text{O}$
	Calcium sulfate	CaSO_4
35	Lead carbonate	PbCO_3
	Magnesium metaborate octahydrate	$\text{Mg}(\text{BO}_2)_2 \cdot 8\text{H}_2\text{O}$
	Magnesium hydroxide	$\text{Mg}(\text{OH})_2$

		Magnesium orthophosphate	$\text{Mg}_3(\text{PO}_4)_2$
		Strontium carbonate	SrCO_3
		Strontium metasilicate	SrSiO_3
		Strontium orthosilicate	SrSiO_4
5		Thorium hydroxide	$\text{Th}(\text{OH})_4$
		Zinc carbonate	ZnCO_3
		Zinc orthophosphate	$\text{Zn}(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$
		Zinc metasilicate	ZnSiO_3
	<u>Blue</u>	Ferric ferrocyanide (Prussian blue)	$\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$
10		Ferrous ferricyanide (Turnbull's blue)	$\text{Fe}_3[\text{Fe}(\text{CN})_6]_2$
		Cupric phosphate	$\text{Cu}_3(\text{PO}_4)_2$
		Copper hydroxide	$\text{Cu}(\text{OH})_2$
		Copper basic carbonate	$2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$
15	<u>Violet</u>	Chromium orthophosphate hexahydrate	$\text{CrPO}_4 \cdot 6\text{H}_2\text{O}$
	<u>Red</u>	Mercurous iodide	Hg_2I_2
		Mercuric iodide	HgI_2
		Silver chromate	AgCrO_4
		Bismuth iodide	BiI_2
20			BiI_3
		Cobalt carbonate	CoCO_3
		Cobalt orthophosphate octahydrate	$\text{Co}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$
		Cobalt ferricyanide	$\text{Co}[\text{Fe}(\text{CN})_6]_2$
		Copper ferrocyanide	$\text{Cu}_2\text{Fe}(\text{CN})_6 \cdot 2\text{H}_2\text{O}$
25		Stannous iodide	SnI_2
	<u>Pink</u>	Cobalt phosphate	$\text{Co}_3(\text{PO}_4)_2$
		Manganese ammonium phosphate	$\text{Mn}(\text{NH}_4)\text{PO}_4$
		Cobalt orthophosphate dihydrate	$\text{Co}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$
		Manganese carbonate	MnCO_3
30	<u>Yellow</u>	Cadmium sulfate	CdS
		Cadmium molybdate	CdMoO_4
		Barium chromate	BaCrO_4
		Antimony sulfide	Sb_2S_3
		Calcium chromate	$\text{CaCrO}_4 \cdot 2\text{H}_2\text{O}$
35		Copper ferricyanide	$\text{Cu}_3[\text{Fe}(\text{CN})_6]_2 \cdot 14\text{H}_2\text{O}$
		Lead chromate	PbCrO_4
		Lead iodide	PbI_2

	Mercurous carbonate	Hg_2CO_3
	Molybdenum metaphosphate	$\text{Mo}(\text{PO}_3)_6$
	Silver iodide	AgI
	Silver orthophosphate	Ag_3PO_4
5	Tin sulfide	SnS_2
	<u>Green</u> Chromium pyrophosphate	$\text{Cr}_4(\text{P}_2\text{O}_7)_3$
	Copper metaborate	$\text{Cu}(\text{BO}_2)_2$
	Copper basic carbonate	$\text{CuCO}_3\text{Cu}(\text{OH})_2$
	Nickel orthophosphate octahydrate	$\text{Ni}(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$
10	Nickel carbonate	NiCO_3
	Chromic phosphate	CrPO_4
	<u>Black</u> Copper sulfide	CuS

One of ordinary skill in the art would know
 15 which salts would form each precipitate.

Preferred examples of soluble salts that form an insoluble precipitate include CaCl_2 and Na_2SiO_3 , yielding the precipitate CaSiO_3 (an opaque white filler); BaCl_2 and Na_2SO_4 , yielding BaSO_4 (a white
 20 opaque filler); and CaCl_2 and Na_2CO_3 , forming CaCO_3 (opaque white filler). It should be noted that it is possible to replace a sodium cation with a potassium cation in any of the soluble salts. Examples of green precipitate fillers are NiCO_3 , formed by the combination
 25 of the aqueous salts NiCl_2 and Na_2CO_3 ; copper carbonate (CuCO_3), from cuprous chloride (Cu_2Cl_2) and sodium carbonate; and chromic phosphate (CrPO_4), from chromic chloride (CrCl_3) and sodium phosphate (Na_3PO_4). The preferred precipitate filler material is calcium
 30 carbonate (CaCO_3). Calcium carbonate can be formed, for example, by having one solution of calcium chloride and the other solution of sodium or potassium carbonate. In all of the insoluble precipitates that are formed, the order of use of the soluble salts is not important.

35 The concentration of salt or salts in the aqueous solution can vary from about 1% to about 40%, depending upon the solubility of the salt in an aqueous

system, the temperature of the process, and the amount of filler desired. Preferably, the concentration of salt or salts in the aqueous solution should be as saturated as the solubility characteristics and the temperature of the process permit so as to maximize the filler content of the resulting filled, never-dried pulp fibers. When using colored or pigmented filler precipitates, it is desirable not to maximize the amount of filler in the cell wall of the never-dried fibers.

10 The inventive process allows for the improved retention of mechanical properties of never-dried pulp when the cell wall is loaded with a precipitated filler in situ. When never-dried pulp was filled with NiCO_3 , formed from the soluble salts NiCl_2 and NaCO_3 , the
15 nickel precipitate can be visualized by electron dispersion analysis (EDAX).

Loaded, never-dried pulps were washed on a wire screen (mesh #100) with tap water. Microscopic observation of the washed, never-dried pulp indicated
20 that this procedure was not efficient enough to completely remove excess filler material from around internally filled, never-dried fibers. Handsheet formation, drying, and conditioning were done in accordance with TAPPI standards. See TAPPI Official
25 Test Method T 205 om-81 from the American National Standard, April 1982.

Figure 1a shows the location of nickel, and Figure 1b shows the nickel distribution. The white dots in Figure 1b represent nickel, and the higher density of
30 the white dots enables the fiber cell wall to be visualized. Figures 2a, 2b and 2c show different aspects of a cross section of a never-dried pulp fiber loaded with nickel carbonate filler material by a process described herein. Figure 2a shows the surface
35 of the filled, never-dried pulp fibers with essentially zero nickel present in the third box from the right. Figure 2b shows a high nickel level strongly above

background in a peak in the third box from the right for the cell wall areas of the fibers. Figure 2c shows the nickel concentration in the lumen of the filled, never-dried pulp fiber with very little nickel present.

5 Paper made from never-dried fibers that have been loaded in the cell wall pores with precipitate-type filler material can be used for a wide variety of applications. The following are some of the widest categories, bearing in mind there are also many
10 specialty products which are produced in smaller quantities.

 Fine papers are a broad class of papers used for printing and writing. Generally, fine papers contain fillers. One advantage of feeding the filled,
15 never-dried pulp fibers, filled within their cell wall to a paper machine used in making fine paper, rather than the usual mixture of separate fiber and filler, is a greater retention of the filler material within the fibers. This leads to better control of properties and
20 cleaner machine operation. In addition to the paper being stronger than a corresponding paper conventionally filled with the same concentration of filler material, the paper made from cell wall filled, never-dried pulp exhibits less "two-sidedness." Two-sidedness is due to
25 an unequal distribution of filler across the thickness of the sheet. Further, there is less tendency for the filler to "dust off" from the sheet during the converting processes of wetting and slitting.

 Unbleached kraft pulp is used for paper
30 products such as paper bags and wrapping papers because of its high strength. However, it has a low brightness, thus making it both unattractive and a poor substrate for printing paper. Never-dried, unbleached kraft pulp fibers with filled cell walls improve the brightness of
35 the paper produced and less strength is lost from filler loading than with conventional loading techniques and dried pulp fibers.

Most newsprint is currently made from a mixture of mechanical and chemical pulp without filler. There is a demand for such products of lower basis weight (pulp weight per unit area). One of the barriers to achieving substantial decreases in basis weight is that such changes reduce the opacity of the sheet. Filler is not currently added to offset the loss in opacity for various reasons, including the loss of strength it causes in the sheet and the "messiness" it imparts to the papermaking operation. Using cell wall filled, never-dried pulp fibers, the newsprint problems are reduced and newsprint can be made with improved levels of opacity.

The following examples are set forth to illustrate the inventive method and compositions produced by the inventive method and not to limit the scope of the invention.

EXAMPLE 1

This example illustrates a comparison using softwood never-dried pulp from western hemlock, comparing the properties of the paper made from the inventive process and a conventional process. In each case, the pulp was beaten to 400 CSF before treatment. For the inventive process, a sample of never-dried pulp (10 g) was dispersed in a 5%, 10%, 20%, or 35% solution of CaCl_2 in 500 mL of water. After 30 minutes, the CaCl_2 -impregnated fibers were collected by filtration under reduced pressure and redispersed in a saturated Na_2CO_3 solution (1,000 mL). After one hour, the dispersion was filtered into a 200 mesh wire screen and then washed with water until the filtrate was clear.

The never-dried pulps used for the preparation of conventionally loaded papers were also washed over a 200 mesh wire screen five times at 0.5% consistency. The conventionally filled pulp had its pH value of 8.0 adjusted using NaOH. A retention aid (Reten 210,

Hercules Corp.) was added at various rates (0.5-1.5 lb/ton of pulp) to achieve the appropriate retention of the commercial CaCO_3 slurry. The time of agitation was one minute.

5 Sheets were made with both the conventional pulp and filler mixes and cell wall loaded, never-dried pulp by using TAPPI standard sheetmaking conditions. The filler (CaCO_3) content of the sheets was calculated by the ash content, as determined by the standard TAPPI
10 procedure, except that the temperature of the furnace was 575°C.

In Figures 3 and 4, the papers made from the cell wall loaded, never-dried pulp are shown by the closed circles. The papers made by conventional
15 techniques are shown by the open points.

Figure 3 shows the effect of filler level on the tensile index for conventional and cell wall loaded, never-dried pulp. These data indicate that at equal CaCO_3 filler concentrations, the sheets made with fibers
20 filled by the inventive process have tensile properties superior to those made by a conventional process.

Similar comparative data are obtained in Figure 4, where the burst strength of the papers is measured. Figure 4 is a plot of the burst index versus
25 filler concentration in the paper for both types of filled papers. These data demonstrate the superior burst strength values obtained using fibers filled by the inventive process.

These data indicate that at equal levels of
30 filler concentration, the inventive process allows more filler to be added at the same paper strength or it provides for a higher level of strength at the same concentration of filler. Filled paper sells for approximately \$1,000/ton or \$0.50/lb when pulp costs
35 \$500/ton and filler costs \$200/ton. Thus, every additional percent of filler that can be placed in a sheet instead of fiber represents a significant

manufacturing cost savings of about \$3-\$4/ton to the papermaker. Moreover, the inventive process does not require a retention aid and thus the formation of the paper can be improved. Thus, when using a softwood
5 kraft pulp, the inventive process improves the strength properties of the resulting paper.

EXAMPLE 2

This example illustrates a comparison of
10 various mechanical properties of paper made with never-dried, cell wall loaded pulps from red alder versus never-dried red alder pulps combined with filler by conventional means versus once-dried red alder pulp fibers filled by the inventive process. In each
15 instance, the never-dried pulps were initially beaten to 400 mL CSF prior to filler loading by either technique. The methods used for filling red alder pulps by the inventive process or combining by the conventional techniques are described in Example 1. Calcium
20 carbonate was provided as a slurry for the conventional technique or precipitated in situ according to the inventive process. The concentration of filler was determined from the ash content.

Figures 5, 6, and 7 compare the tear index,
25 burst index, and tensile index, respectively, comparing red alder never-dried pulps filled by the inventive process or by the conventional technique. In each illustration, the ash content indicates the percent of filler in the paper. Therefore, in each figure it is
30 possible to compare the tear index, burst index, and tensile index of paper made from each type of filled fiber at equivalent filler concentrations.

In Figures 5, 6, and 7, the upper line with the higher tear burst or tensile indices is for papers
35 made with fibers filled by the inventive process. The squares represent never-dried pulp fibers filled wherein the sequence of solution addition is first calcium

chloride followed by sodium carbonate and the circles have the reverse sequence of sodium carbonate followed by calcium chloride. The lower line with the X-shaped points represents once-dried pulp fibers filled by the inventive process. The lower line with the diamond points represents conventionally loaded, never-dried pulps.

In each instance, the strength of the resulting paper, as measured by tear index, burst index, and tensile index, was higher for the inventive process using never-dried pulp fibers. Further, the order of addition of the two solutions is not important.

EXAMPLE 3

This example illustrates a comparison of spruce CTMP (chemithermomechanical pulp) never-dried pulp fibers filled by the inventive process or by conventional techniques. The never-dried fibers were initially beaten to 400 mL CSF. The inventive process and the conventional process used to fill the fibers are described in Example 1. Figures 8, 9, and 10 illustrate the tear index, burst index, and tensile index, respectively, of papers made from spruce CTMP never-dried pulp fibers filled by the inventive process and by the conventional technique. In each of the three figures, the inventive process is illustrated by squares and the conventional admixture process by circles.

A characteristic of spruce CTMP pulp is that the tensile, burst, and tear indices decrease faster with increasing ash contents (i.e., increasing filler contents). For each strength parameter, the paper made from never-dried pulp fibers filled by the inventive process demonstrated increased strength as compared with paper whose fibers were filled by conventional techniques.

EXAMPLE 4

This example compares bagasse pulps derived from sugarcane fibers comparing bleached and unbleached, never-dried pulps filled by the inventive method to
5 bleached pulps that were once dried and filled by the inventive method to conventionally loaded bleached pulps. The processes used to make each paper and to combine the fibers and the filler are described in Example 1.

10 Figures 11, 12, and 13 illustrate the tear index, burst index, and tensile index, respectively, of each of the three types of paper. The squares illustrate the inventive process, wherein the data from paper made from bleached, never-dried pulp fibers are
15 indicated by filled-in squares and unbleached, never-dried pulp fibers by open squares. The data from paper made from never-dried bagasse fibers loaded by the conventional process is illustrated by the triangles. The data from papers made from bleached, never-dried
20 pulp fibers are shown by closed diamonds and unbleached, never-dried pulp fibers by open diamonds. Paper made from once-dried, bleached pulp and filled by the inventive process is shown by the triangles.

As shown in Figures 11, 12, and 13, paper made
25 with never-dried bagasse pulp fibers filled by the inventive process demonstrated superior strength characteristics at each concentration of filler tested.

EXAMPLE 5

30 This example illustrates a comparison of paper tensile strength characteristics when using fibers filled by the inventive process with the lumen-loading process as described in United States Patent No. 4,510,020, the disclosure of which is incorporated by
35 reference herein. Figure 14 illustrates the relative decrease in tensile strength of paper expressed as a percentage versus the filler content expressed as a

percentage with red alder never-dried pulps, bagasse never-dried pulps, and spruce CTMP never-dried pulps filled by the inventive process as compared with lumen-loading techniques using softwoods, as derived from
5 Miller et al. in Proceedings 1983 TAPPI International Paper Physic Conference, Harwichport, p. 237 ("Miller et al."), and Green et al., Pulp & Paper Canada, 83:T203 (1982) ("Green et al.").

Larger amounts of filler were loaded within
10 hardwood never-dried pulp fibers using the inventive process when compared with Green et al.'s data for softwoods and similar amounts when compared with the Miller et al. softwoods. However, it should be noted that Miller et al. conducted their experiments with the
15 inclusion of 2% PEI. PEI (polyethyleneimine) is a polycationic polymer which can form ionic bonds between the fibers in paper and acts to strengthen paper. PEI will function to flocculate the very fine filler particles within the lumen. The agglomeration of filler
20 particles into larger masses improves the retention of filler inside the lumen, thus minimizing unloading mechanisms. We were able to achieve almost 40% filler loading with bagasse never-dried pulps, but at the expense of mechanical properties. The relative decrease
25 of tensile strength of the inventive process showed the same pattern as the Green et al. data with softwood fibers. Miller et al.'s attempt showed encouraging results, but the presence of 2% PEI may have added significantly to the strength of the resulting paper.

30 In Figure 14, the open circles indicate red alder never-dried pulps filled by the inventive process, the open diamonds represent bagasse pulps filled by the inventive process, the filled circles represent spruce CTMP never-dried pulps filled by the inventive process,
35 the closed triangles represent the data in Miller et al., and the X figures represent the data in Green et al.

EXAMPLE 6

This example illustrates how never-dried eucalyptus pulp (a hardwood pulp) can be filled with aluminum hydroxide in situ. Eucalyptus pulp was dispersed in a first solution containing the soluble salt aluminum sulfate. The first solution contained a saturated concentration of aluminum sulfate at room temperature. The first solution was removed after five minutes by filtering the pulp. This also removes the first solution from the pulp lumens.

A second solution containing 20% (w/v) sodium hydroxide was used to disperse the pulp fibers. This formed aluminum hydroxide precipitate~~s~~ predominantly in the cell wall of the fibers.

Paper was made from the fibers filled with aluminum hydroxide filler. The amount of filler in the paper was 9% as determined by ash content of Al_2O_3 (alumina).

20

EXAMPLE 7

This example illustrates the effect of beating filled, never-dried fiber and the effect of different beating conditions. Eucalyptus (hardwood) never-dried pulp was filled with CaCO_3 by the inventive process as described herein. The unbeaten, never-dried pulp had a Canadian Standard Freeness (CSF) of 570 mL. A sample of the filled, never-dried pulp fibers was first beaten for 10,000 revolutions in a PFI mill (beating apparatus). The CSF value was 416 mL. The pulp was then formed into a crude first sheet by filtration onto a wire screen. The ash content of the first sheet was 43%. The pulp was then redispersed in water and refiltered to form a second sheet. The ash content of the second sheet was 38%. This process of redispersion and filtration was repeated three more times. The ash contents of the third, fourth, and fifth sheets were 34%, 36%, and 34%,

respectively. Thus, approximately only 7%-9% of the filler was located outside the cell wall, even after beating for 10,000 revolutions. That is, the filler mainly stays in the cell wall during beating.

5 The entire procedure was repeated; except this time the filled, never-dried pulp fibers were first beaten for 20,000 revolutions, as described above. The CSF value was 366 mL. The first filtered sheet had 46% filler, the second sheet 41% filler, and the third sheet
10 38% filler. Thus, approximately only 8% filler was located outside of the cell wall even after beating for 20,000 revolutions.

 Moreover, it is known that the pulp fibers filled by the lumen-loading technique will lose most of
15 the filler upon beating. The inventive filling process, by contrast, does not lose an excessive amount of the filler upon beating.

 From the foregoing, it will be appreciated that, although specific embodiments of the invention
20 have been described herein for purposes of illustration, various modification may be made without deviating from the spirit and scope of the invention.

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Claims

I claim:

1. A filled paper composition comprising in situ filled, never-dried fibers wherein at least 50% of the filler content is located within the cell wall of the fibers and characterized by having increased strength compared to a corresponding conventionally loaded paper containing the same amount of the same filler.

2. The paper composition of claim 1 wherein the cellulose fibers are derived from hardwoods, softwoods, annual plants, and combinations thereof.

3. The paper composition of claim 1 wherein the filler is characterized as an insoluble precipitate in an aqueous system.

4. The paper composition of claim 1, further comprising a coloring agent wherein the coloring agent is a colored precipitate that functions as a filler.

5. The paper composition of claim 4 wherein the colored filler is selected from the group consisting of blue, violet, red, pink, yellow, green, and black precipitates from Table 1 and combinations thereof.

6. The paper composition of claim 1 wherein the paper is selected from the group consisting of unbleached kraft paper, bleached kraft paper, fine printing paper, fine writing paper, bleached and unbleached sulfite paper, and lightweight newsprint paper.

7. An unbleached kraft paper in which substantially all of the filler is located within the cell wall of the fibers, said paper having increased tensile

strength compared to corresponding conventionally loaded paper containing the same amount of the same filler.

8. A bleached kraft paper in which substantially all of the filler is located within the cell wall of the fibers, said paper having increased tensile strength compared to corresponding conventionally loaded paper containing the same amount of the same filler.

9. A fine printing or writing paper in which substantially all of the filler is located within the cell wall of the fibers, said paper having increased tensile strength compared to corresponding conventionally loaded paper containing the same amount of the same filler.

10. A lightweight newsprint paper in which substantially all of the filler is located within the cell wall of the fibers, said paper having increased tensile strength compared to corresponding conventionally loaded paper containing the same amount of the same filler.

11. A process for the production of filled paper wherein the starting pulp is a never-dried pulp, comprising:

immersing the never-dried pulp in a first solution wherein the first solution comprises a soluble salt or salts;

filtering the pulp from the first solution;

reimmersing the never-dried pulp in a second solution wherein the second solution comprises a soluble salt or salts different from the soluble salt or salts of the first solution, and with the proviso that the interaction of the salt or salts from the first solution and the salt or salts from the second solution form an insoluble precipitate that acts as a filler within the cell wall of the never-dried pulp;

filtering and washing the filled, never-dried pulp to form a filled pulp; and

forming paper with the filled pulp.

12. The process of claim 11 wherein the never-dried pulp is derived from hardwoods, softwoods, annual plants, or combinations thereof.

13. The process of claim 11 wherein the insoluble precipitate is selected from the group consisting of precipitates in Table 1 and combinations thereof.

14. A filled paper made from never-dried pulp wherein the filled paper is made from the process comprising:
immersing the never-dried pulp in a first solution wherein the first solution comprises a soluble salt or salts;
filtering the pulp from the first solution;
reimmersing the never-dried pulp in a second solution wherein the second solution comprises a soluble salt or salts different from the soluble salt or salts of the first solution, and with the proviso that the interaction of the salt or salts from the first solution and the salt or salts from the second solution form an insoluble precipitate that acts as a filler within the cell wall of the never-dried pulp;
filtering and washing the filled never-dried pulp to form a filled pulp; and
forming paper with the filled pulp.

15. The filled paper of claim 14 wherein the never-dried pulp is derived from hardwoods, softwoods, annual plants, or combinations thereof.

16. The filled paper of claim 14 wherein the insoluble precipitate is selected from the group consisting of precipitates in Table 1.

17. A filled pulp fiber comprising filler and pulp wherein the filler comprises an insoluble precipitate and wherein the filler is located within the cell wall of the pulp fiber.

18. The filled, never-dried cellulose pulp fiber of claim 19 wherein the insoluble precipitate is calcium carbonate.

19. A filled pulp fiber wherein the filled pulp fiber is made from the process comprising:

immersing a never-dried pulp in a first solution wherein the first solution comprises a soluble salt or salts;

filtering the pulp from the first solution;

reimmersing the never-dried pulp in a second solution wherein the second solution comprises a salt or salts different from the soluble salt or salts of the first solution and with the proviso that the interaction of the salt or salts from the first solution and the salt or salts from the second solution form an insoluble precipitate that acts as a filler within the cell wall of the never-dried pulp; and

filtering and washing the filled never-dried pulp into a filled pulp fiber.

20. The filled pulp fiber of claim 21, further comprising drying the filled pulp fiber after the filtering and washing step.

21. The filled pulp fiber of claim 19 wherein the never-dried pulp is derived from hardwoods, softwoods, annual plants, or combinations thereof.

22. The filled pulp fiber of claim 21 wherein the insoluble precipitate is selected from the group consisting of precipitates listed in Table 1.

23. The filled pulp fiber of claim 19 wherein the filler is pigmented.

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FIG. 1A

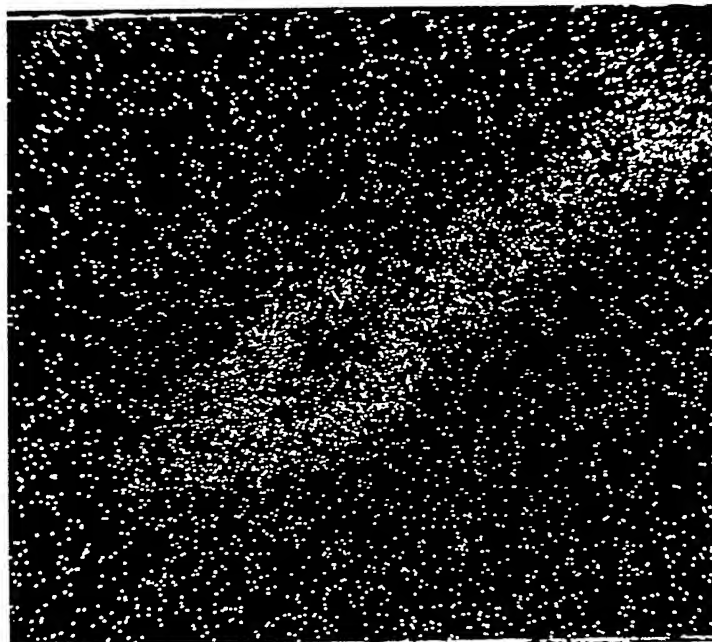


FIG. 1B

SUBSTITUTE SHEET

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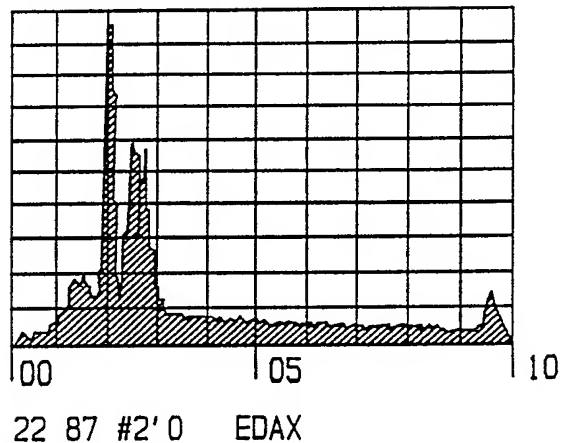


FIG.2a

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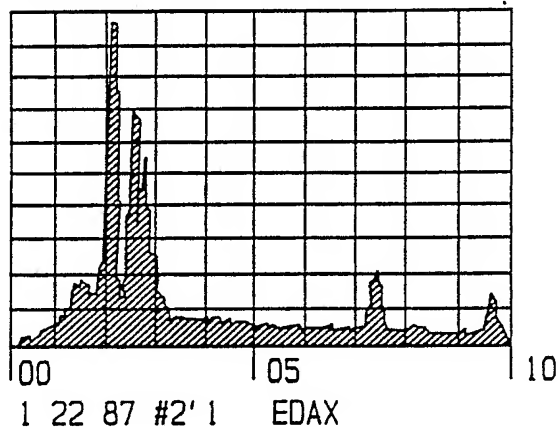


FIG.2b

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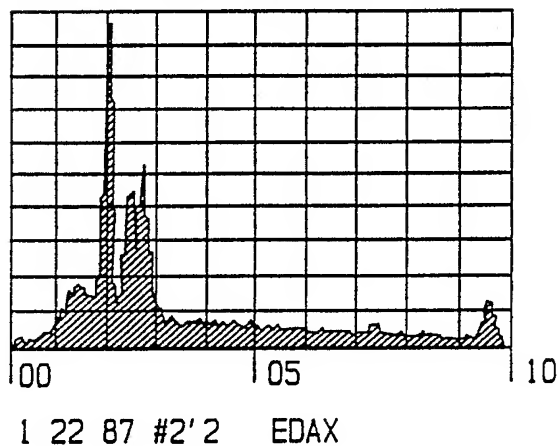
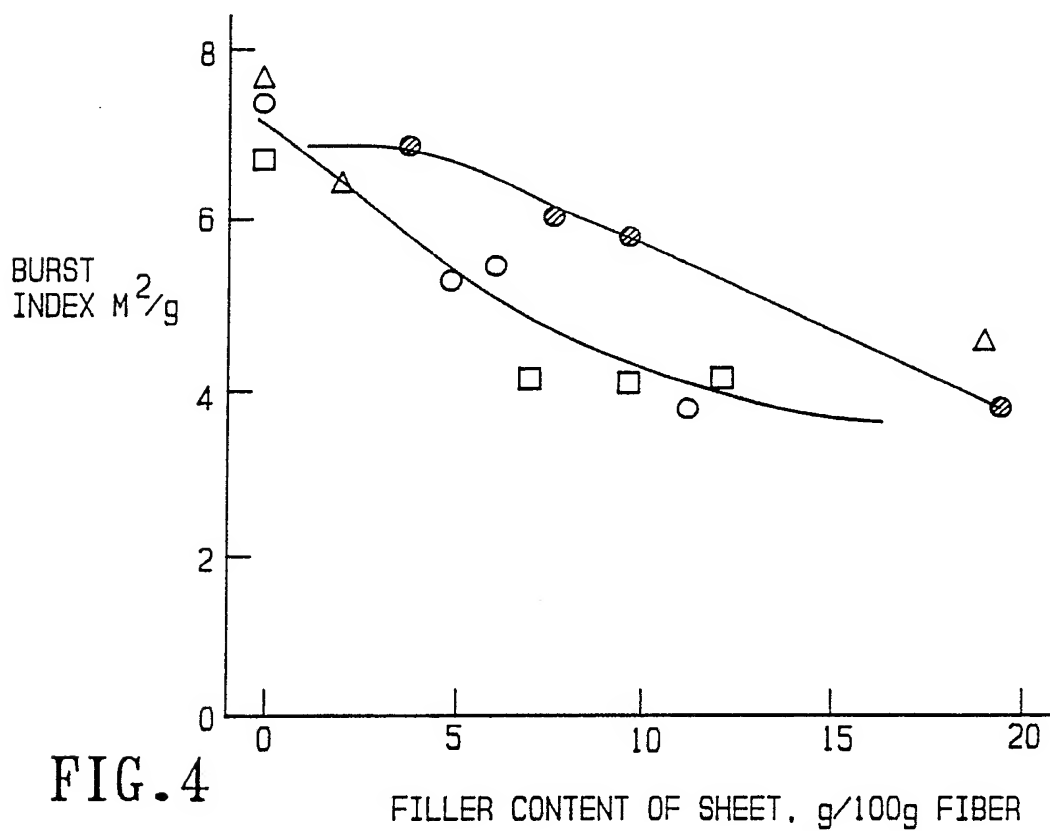
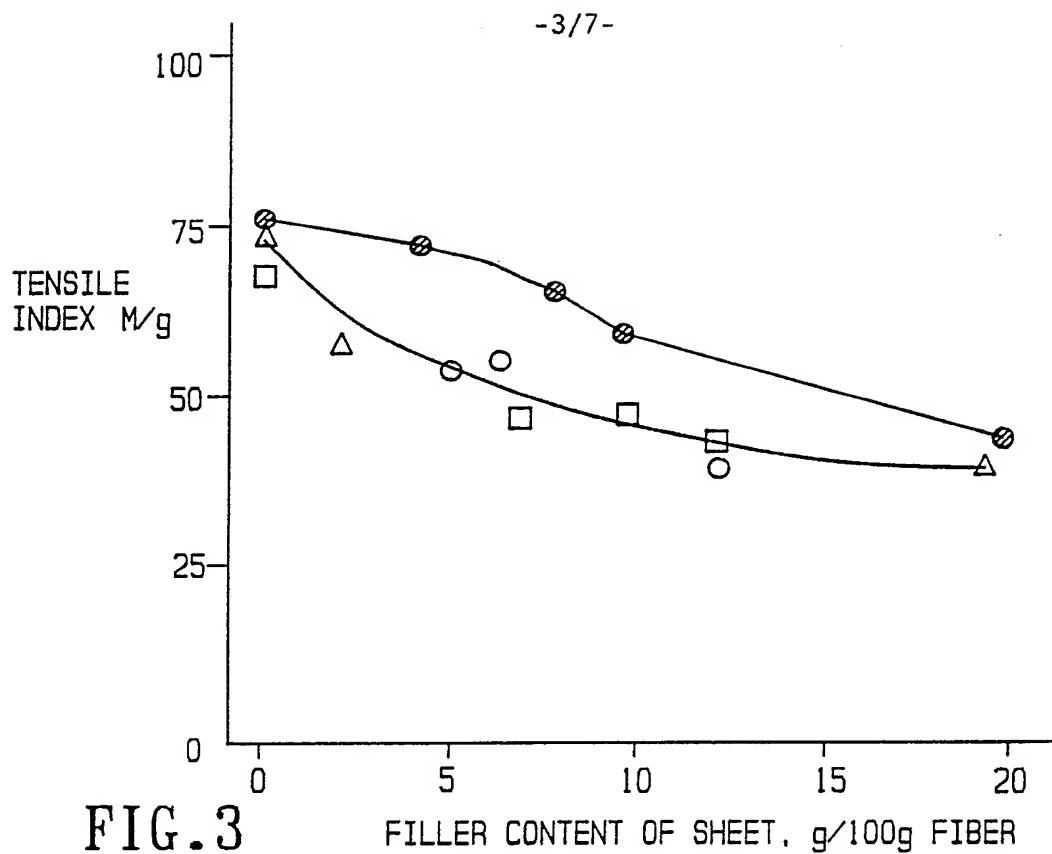
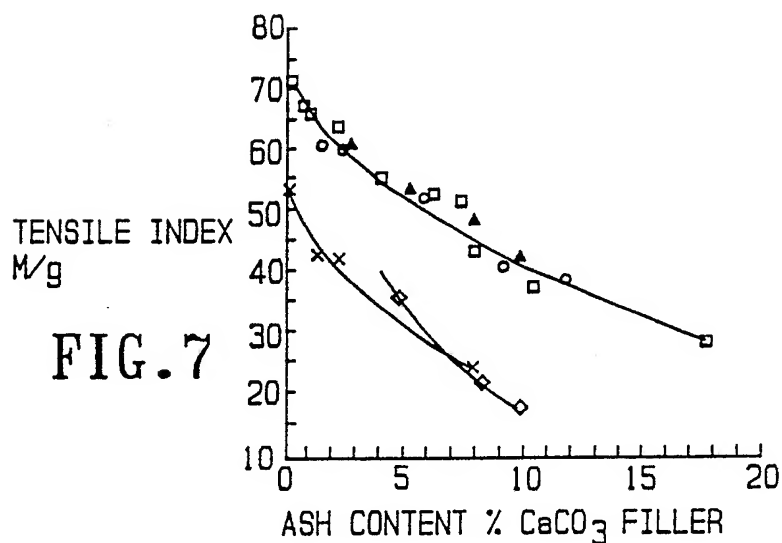
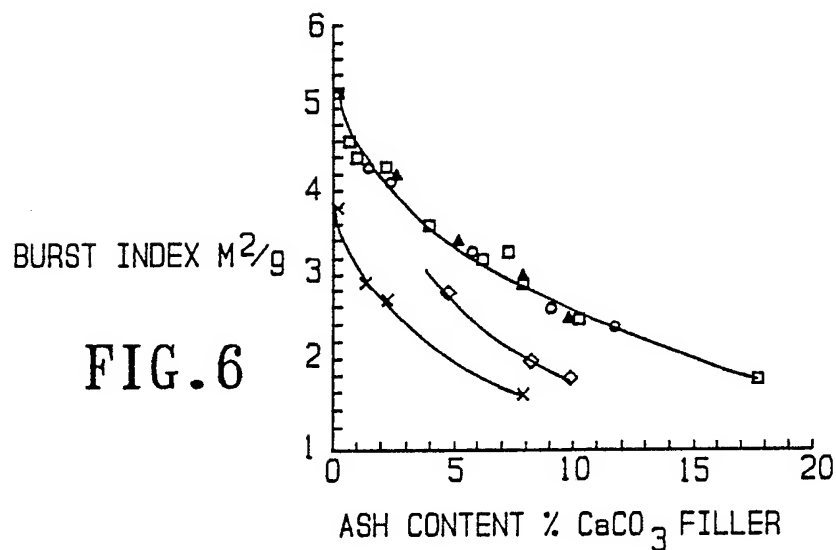
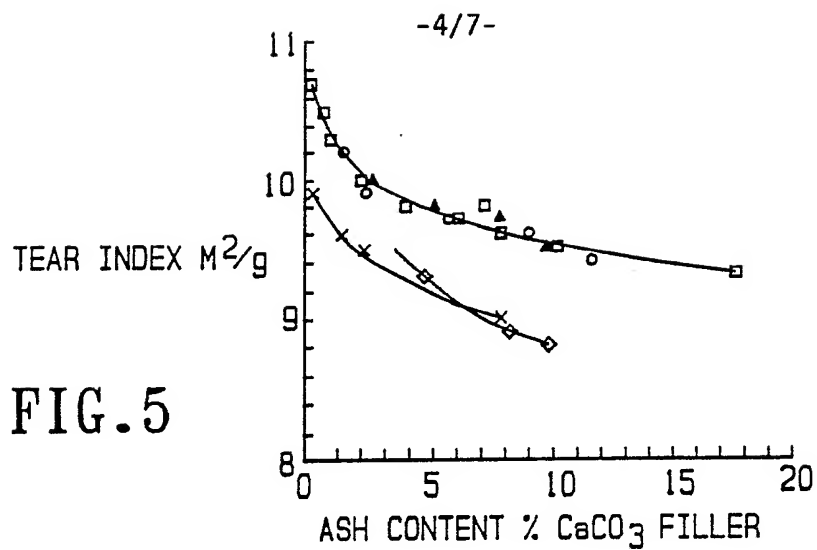


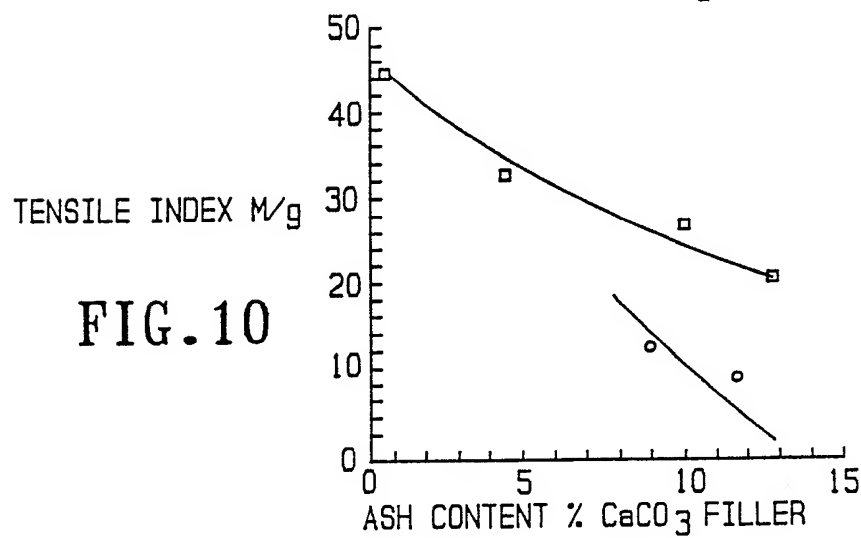
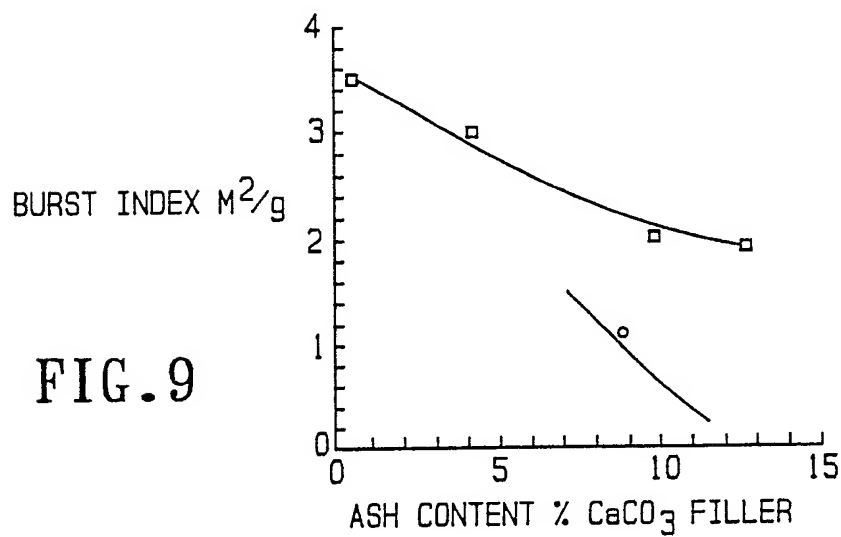
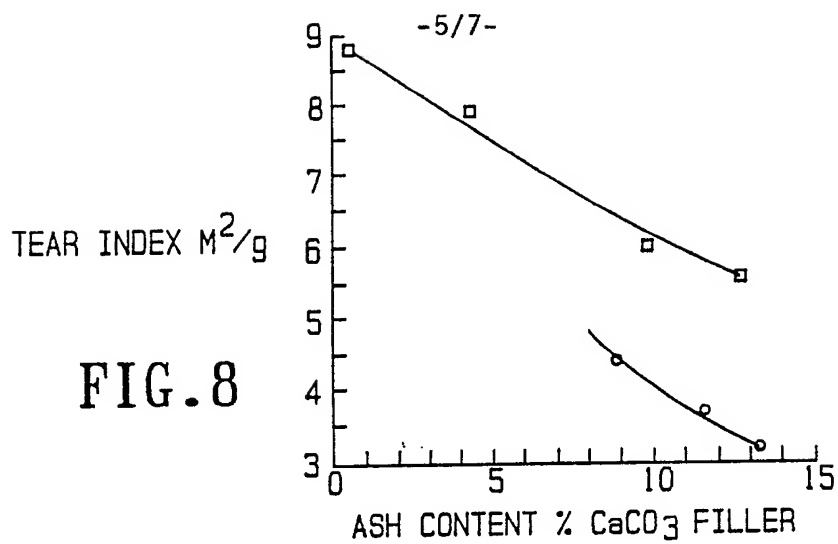
FIG.2c

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TEAR INDEX $M^{2/g}$

FIG. 11

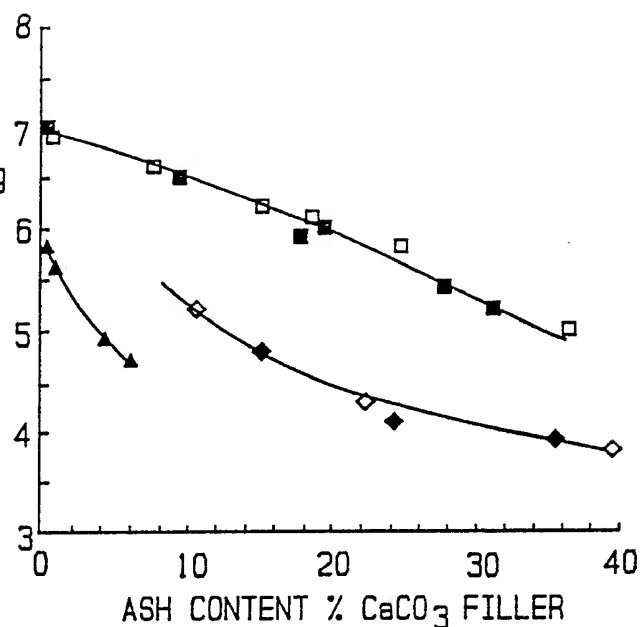
BURST INDEX $M^{2/g}$

FIG. 12

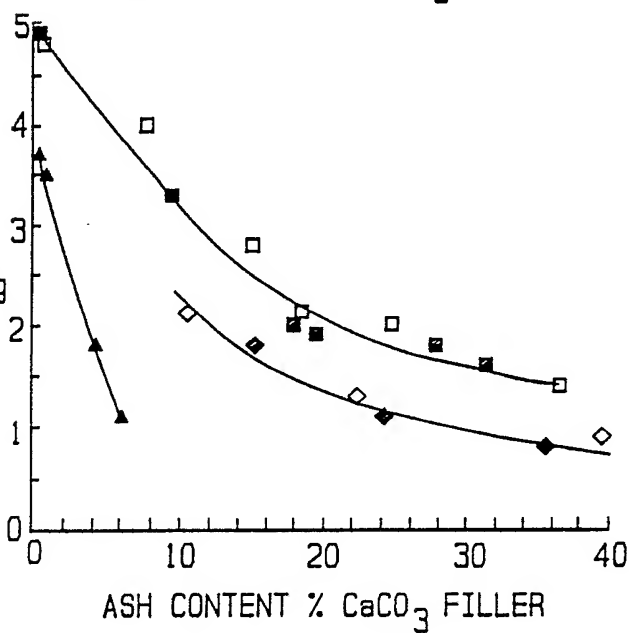
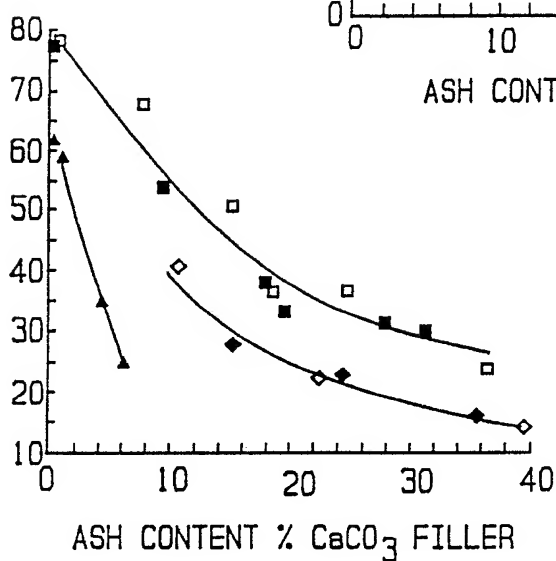
TENSILE
INDEX
 M/g

FIG. 13



-7/7-

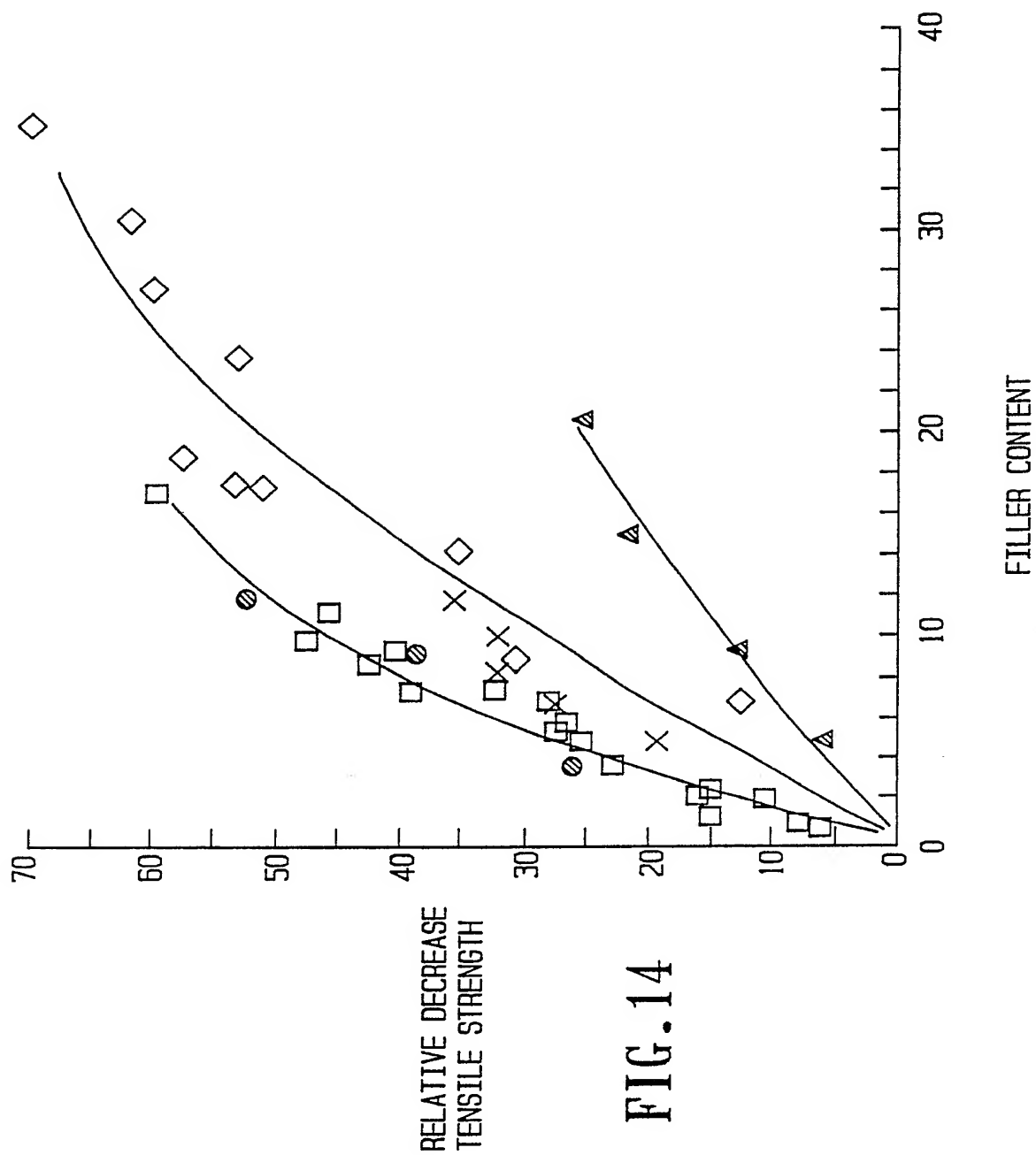


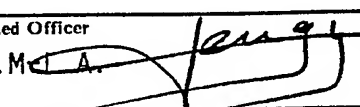
FIG. 14

SUBSTITUTE SHEET

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 90/04138

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC Int.Cl. 5 D21H17/70 ; D21C9/00		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int.Cl. 5	D21H ; D21C ; D21D	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
Y	EP,A,0042234 (PULP AND PAPER RESEARCH INSTITUTE OF CANADA) 23 December 1981 see the whole document	1-3, 6-12, 14, 15, 17-21, 23
Y	& US,A,4510020 (H.V.GREEN ET AL.) (cited in the application) ---	
Y	US,A,2599093 (W.L.CRAIG) 03 June 1952 see the whole document	1-3, 6-12, 14, 15, 17-21, 23
A	WO,A,8604370 (G.GAVELIN) 31 July 1986 see the whole document ---	
A	US,A,2583548 (W.L.CRAIG) 29 January 1952 (cited in the application) ---	
¹⁰ Special categories of cited documents : ¹⁰ "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such docu- ments, such combination being obvious to a person skilled in the art. "&" document member of the same patent family		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
09 NOVEMBER 1990	27 NOV 1990	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	SONGY O.M. A. 	

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

PCT/US 90/04138

SA 39226

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

09/11/90

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0042234	23-12-81	US-A- 4510020 CA-A- 1152266 JP-A- 57061799	09-04-85 23-08-83 14-04-82
US-A-2599093		None	
WO-A-8604370	31-07-86	SE-B- 455318 DE-T- 3590715 EP-A, B 0209538 GB-A, B 2181464 SE-A- 8500162	04-07-88 29-01-87 28-01-87 23-04-87 16-07-86
US-A-2583548		None	